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Experimental Determination of Minimum Miscibility Pressure

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Abstract

Minimum miscibility pressure (MMP) plays a great role in determining the displacement efficiency of different gas injection processes. Experimental techniques for MMP determination include industrially recommended slim tube, vanishing interfacial tension (VIT) and rising bubble apparatus (RBA). In this paper, MMP measurement study using slim tube and VIT experimental techniques for two different crude oil samples (M and N) both in live and stock tank oil forms is being presented. VIT measured MMP values for both 'M' and 'N' live crude oils were close to slim tube determined MMP values with 6.4 and 5 % deviation respectively. Whereas for both oil samples in stock tank oil form, VIT measured MMP showed a higher unacceptable deviation from slim tube determined MMP. This higher difference appears to be related to high stabilized crude oil heavier fraction and lack of multiple contacts miscibility. None of the different nine deployed crude oil – CO_2 MMP computing correlations could result in reliable MMP, close to slim tube determined MMP. Since VIT determined MMP values for both considered live crude oils are in close match with slim tube determined MMP values, it confirms reliable, reproducible, rapid and cheap alternative for live crude oil MMP determination. Whereas VIT MMP determination for stock tank oil case needed further investigation about stabilization / destabilization mechanism of oil heavier ends and multiple contacts miscibility development issues.

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Keywords: Minimum miscibility pressure, Interfacial tension, Multiple contacts miscibility, Heavier ends stability

1. Introduction

Miscible gas injection processes have become widely used technique for the enhanced oil recovery (EOR) or improved oil recovery (IOR) throughout the world. In miscible gas flooding, the main objective is to miscible displace the trapped oil fractions with the help of gaseous solvent. To increase the displacement efficiency and improve the oil recovery, the knowledge of minimum miscibility pressure (MMP) is essential. At MMP, the interfacial tension across the interface between the concurrent streams (injected gas and reservoir fluid) approaches zero, which results in potential transfer of molecules across the interface leading to mutual miscibility and homogeneous fluid formation [1, 2]. There are a number of experimental techniques for the determination of MMP like slim tube, vanishing interfacial tension (VIT) and rising bubble apparatus (RBA). A number of researchers deployed the slim tube for different gas – oil systems for determination of MMP and established different criteria for its prediction. Elasharkawy et al. conducted the MMP comparative study, determined using RBA and slim tube for twelve different oils and CO_2 systems. They referred the slim tube as non-standardized method for MMP determination with respect to both operating procedure and design, even it was industrially accepted and reliable one [3].

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Nomenclature

MMP	Minimum Miscibility Pressure
VIT	Vanishing Interfacial Tension
IFT	Interfacial Tension
EOR	Enhanced Oil Recovery
GOR	Gas Oil Ratio
RBA	Rising Bubble Apparatus

Holm et al. defined the MMP against 80 % oil recovery at gas breakthrough [4]. Graue et al. investigated the effect of light gas components in CO_2 injected stream on recovery performance and designed a miscibility criterion of 90 % recovery of original oil in place (OOIP) at 1.2 PV of injected gas [5]. Yelling and Metcalfe et al. referred the displacement as miscible one near 1.2 PV of injected gas and correlated the crude oil color degradation from dark black to yellow to multi-contact miscibility development [6]. Randal et al. suggested the use of longer length and small diameter slim tube coil and low solvent injection rate for slim tube experiments to avoid the compositional variations, transition zone length and viscous fingering effects [7]. Omole et al. conducted the slim tube experiments using different sand packs lengths and found no effect of it on measured MMP [8]. Flock et al. studied the effect of slim tube coil length and solvent injection rate on MMP determination [9].

VIT is another experimental technique for determination of MMP. The idea of this technique is to predict the miscibility conditions by measuring the interfacial tension (IFT) across the fluid phases against varying injection pressures or injection gas composition. As IFT approaches zero, there will be no interface across the fluid phases and transfer of molecules take place between fluid bulks that results in miscibility development. Rao et al. utilized this technique to find out the miscibility conditions (minimum miscibility enrichment, MME or minimum miscibility pressure, MMP) for a number of oil – gas systems by varying the injected gas composition and injection pressure respectively [10-14]. Jessen & Orr reviewed this technique and assumed this technique as an unreliable source for MMP determination because of lack of multi-contact miscibility achievement. They pointed out the lack of phase equilibrium establishment for varying composition of gas – oil mixtures utilized in this technique [15, 16]. Rao et al. responded to this criticization by measuring the IFT for a number of gas – oil mixtures at varying oil – gas mixture compositions and constant temperature. They found that measured IFT remained unchanged by varying gas - oil ratio in utilized mixture as phases approached equilibrium [17].

As a result of aforementioned experimental MMP research work, a study for MMP determination using slim tube and VIT experimental techniques is conducted. In it, two reservoir crude oils (M & N) both in live and dead (stock tank oil) forms are being utilized separately and evaluation of experimental MMPs is being carried out. An extensive research work recommended slim tube system with coil length of 24 m and injection rate of 0.1 cc / min was used. The utilized injection solvent for both live and dead crude oils displacement study was pure CO_2. In addition, a comparative evaluation of crude oil – CO_2 MMP computing correlations with slim tube measured MMP was also carried out to find a suitable correlation for accurate MMP prediction.

2. Materials and methodology

2.1. Live crude oil sample preparation

Both of the live crude oil samples used in this study are recombined samples, prepared from effluent streams of production separator (flash gas and liquid). Both streams were mixed in a recombination unit in a specific ratio, so that gas oil ratio (GOR) for produced live oil resembled the one for original reservoir oil. A number of PVT experiments were performed for both produced live crude oils to determine various fluid properties like bubble point pressure (P_b), gas oil ratio (GOR) and oil formation volume factor (B_o). All these properties values were found in close match with calculated ones for original reservoir oil as it is illustrated in Table 1. Whereas, the utilized dead crude oil samples are stock tank oils. The composition detail for both crude oil samples and injection gas is illustrated in Table 2.

Table 1: Comparison of original reservoir fluids properties with produced oils ones for validation purpose

Crude Oil Sample	Reservoir Fluid, P_b (psi)	Produced Oil, P_b (psi)	% Deviation	Reservoir Fluid, GOR (Sm^3/m^3)	Produced Oil, GOR (Sm^3/m^3)	% Deviation	Reservoir Fluid, B_O (rm^3/Sm^3)	Produced Oil, B_O (m^3/m^3)	% Deviation
M	1822	1845	1.2	80.8	83	2.7	1.205	1.232	2.2
N	2010	2042	1.5	121	124.5	2.9	1.415	1.453	2.6

Table 2: Crude oil samples & injection gas composition

Component	Crude Oil M	Crude Oil N	Injection Gas
N_2	0.562	0.22	0
CO_2	0.208	0.33	100
H_2S	0.00	0.00	0.00
C_1	30.193	33.09	0.00
C_2	4.935	6.3	0.00
C_3	4.117	5.80	0.00
i-C_4	1.562	2.32	0.00
n-C_4	3.498	4.18	0.00
i-C_5	1.936	2.44	0.00
n-C_5	2.438	2.47	0.00
C_6	4.118	3.83	0.00
C_{7+}	46.433	39.02	0.00
Total	100.00	100.00	100.00

2.2. Experimental work

2.2.1. VIT experimentation

When two fluids come in contact, interface develops between the phases, which prevents the mutual miscibility. As the interfacial tension across the interface approaches zero, there will be no interface and miscibility develops in all proportions. Therefore, oil recovery can be improved with gas injection at near MMP, corresponds to which IFT reaches zero. VIT is deployed to determine MMPs for considered gas – oil systems by measuring the interfacial tensions at various pressures.

2.2.1.1. *Equipment design and procedure*

The deployed equipment schematic demonstration is shown in Fig.1. The heart of this equipment is optical cell with designed volume of 20 cc. It is a high pressure, high temperature cell with an operating temperature and pressure range of 180 ^{0}C and 700 bar respectively. PAAR DMA 45 was used for oil density measurement. A Ruska pump for injecting the fluids in their respective cylinders and injecting the CO_2 gas inside the optical cell for desired pressure maintaining purpose. A computer with image captures board facility and installed software, based on axisymmetric drop shape analysis (ADSA), for image analysis was utilized.

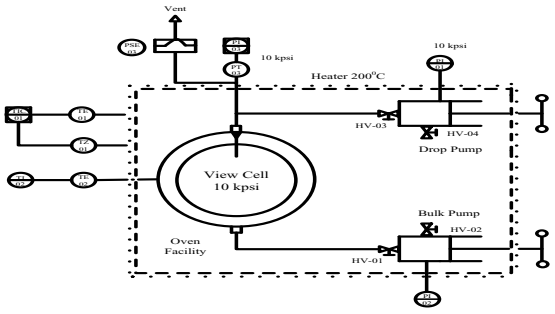

Fig.1: Slim tube apparatus schematic demonstration

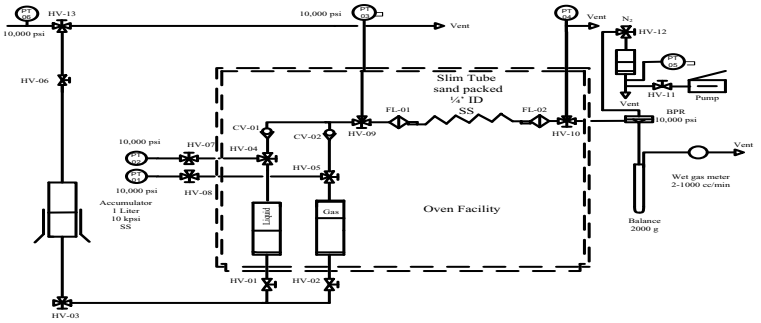

Fig.2: Schematic diagram of interfacial tension apparatus

After finishing the cleaning process, the optical cell was filled with CO_2 gas and it desired pressure was maintained by controlling the CO_2 gas injection using Ruska pump. A hanging pendent drop is introduced through injection needle inside the optical cell at various pressures. Using camera, drop shape is focused and magnified image is captured and saved in computer. Axis drop shape analysis (ADSA) is utilized to analyze drop shapes [18-20]. In it, Laplace capillary equation is solved iteratively to fit the theoretical drop shape to real experimental one for the determination of IFT.

2.2.2. Slim tube experimentation

2.2.2.1. Equipment design and procedure

The slim tube used in this study is shown in Fig.2. A coil length of 24 m with 1/4' outer diameter (OD) enclosed with 100 mesh sand particles in tight helix form was used. Following installations were insured : high pressure floating piston cylinders for storage of injection gas and reservoir oil, oven facility for thermal maintenance and stabilization of fluids at desired temperature, positive displacement syringe pump for fluids displacement, cleaning solvent storage accumulator, back pressure regulator at coil outlet, separator facility for separation of gas and liquid streams from recovered fluid stream, wet gas meter for flashed gas monitoring.

Constant pressure injection of CO_2 at rate of 0.1 cc / min was carried out for both samples in live and stock tank oil forms. The injection was continued till a clear gas break through was observed in recovery versus injected pore volume plot at 1 to 1.2 injection pore volume. After break through, CO_2 injection was stopped and inside coil retained gas and unrecovered oil were measured for displacement efficiency evaluation.

2.3. MMP correlations

In 1974, Holm & Josendal develop the correlation to predict the Co_2 MMP using the reservoir temperature and C_{5+} molecular weight of crude oil. Cronquist also developed MMP correlation based on C_{5+}. Lee J. proposed a reservoir temperature based model for the prediction of MMP using Co_2 vapor pressure. Orr and Jensen approach for MMP is most suitable for low temperature reservoirs. Glaso presented the minimum miscibility correlation based upon the Benham et al. correlation [21]. Astlon proposed a correlation for MMP prediction based on reservoir temperature, molecular weight of C_{5+} oil fractions, volatile and intermediate oil fractions and composition of injected gas stream. Yuan et al. proposed correlation is based on molecular weight of C_{7+} oil fractions, reservoir temperature and the percentages of intermediates fractions (C_2 – C_6) in the oil. Emera & Sarma developed a new correlation for the determination of MMP based on new genetic algorithm (GA). Shokir developed a new model for the prediction of both pure and impure Co_2 displacement. All aforementioned crude oil – CO_2 MMP computing correlations mathematical expressions are given in appendix.

3. Results and discussion

3.1. Slim tube measured MMP

Slim tube recovery and MMP data for both live and dead crude oil samples is demonstrated in Figs. 3, 4, 5 and 6. From plots it is clear that MMP values for samples M and N, both in live and dead form, are 2816.73, 3242.47 and 2303.54, 2602.37 psi respectively. By comparing the MMP values for live and dead crude oil forms

in each sample case, live oil MMP found to be 22.28 % more compared to dead oil MMP for crude oil sample M and 24.6 % for crude oil sample N.

3.2. VIT measured MMP

Same Figs. 3, 4, 5 and 6 include also VIT measured IFT data. By comparing live oil MMPs for each sample, it was found that VIT measured MMP differed the slim tube measured MMP by 181.59 psi for oil sample M and 154.68 psi for oil sample N. Whereas in stock tank oil case this difference increases to 498.3 psi for oil sample M and 438.5 psi for oil sample N. For heavy dead oil, the transfer of very low fraction crude oil light ends into CO_2 gas phase is too low to be enrich enough for solubility with crude oil. In case of stock tank oil with high stabilized heavier ends, this difference can be correlated to lack of multiple contacts miscibility developed between crude oil and gas phases compared to achieved miscibility in slim tube case at respective injection pressure.

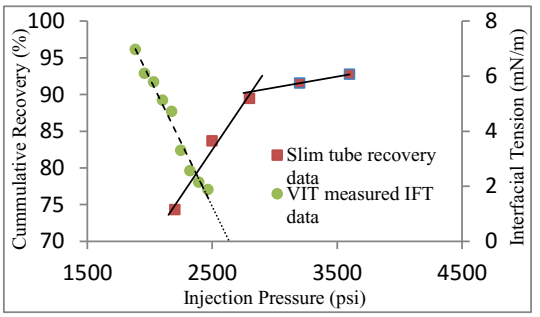

Fig.3: MMP comparison determined using slim tube and interfacial tension method for live crude oil sample M (dot = exp., line = Regr.)

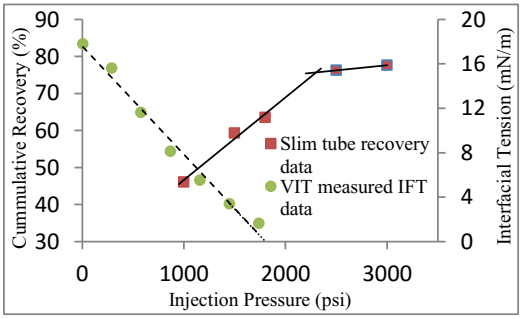

Fig.4: MMP comparison determined using slim tube and interfacial tension method for dead crude oil sample M (dot = exp., line = Regr.)

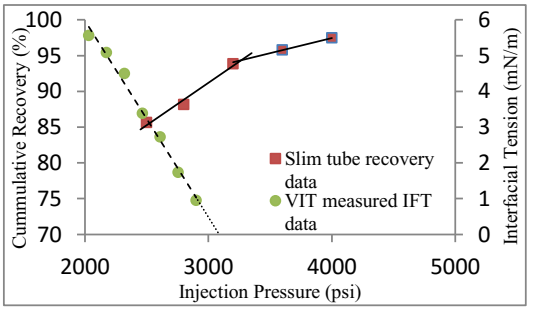

Fig.5: MMP comparison determined using slim tube and interfacial tension method for live crude oil sample N (dot = exp., line = Regr.)

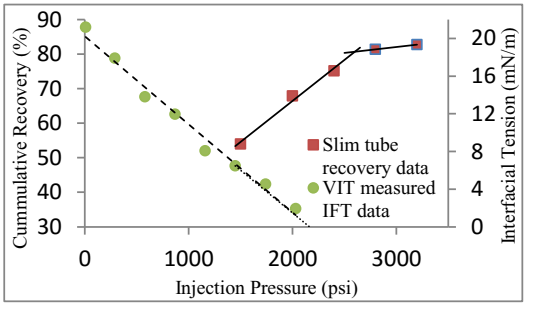

Fig.6: MMP comparison determined using slim tube and interfacial tension method for dead crude oil sample N (dot = exp., line = Regr.)

3.3. Correlations calculated MMP

Each correlation calculated MMP value with its deviation from experimental determined slim tube MMP value is given in table 3. From correlations calculated MMP data analysis, it is clear that in case of sample M, no correlation can predict MMP close to slim tube measured MMP. Whereas for sample N, the correlation to calculate the MMP, most close to slim tube determined MMP value, is the Shokir correlation with 8.85 % deviation.

Table 3: Comparison of slim tube measured MMP with existing correlations predicted MMPs

Oil Sample	Slim Tube MMP (psi)	Cronquist		Alston		Glaso		Lee		Yelling & Metcalfe		Orr & Jessen		Emera & Sarma		Yuan et al.		Shokir	
		Cal. (psi)	% Dev.	Cal. (psi)	% Dev.	Cal. (psi)	% Dev.	Cal. (psi)	% Dev.	Cal. (psi)	% Dev.	Cal. (psi)	% Dev.	Cal. (psi)	% Dev.	Cal. (psi)	% Dev.	Cal. (psi)	% Dev.
M	2816.73	767.45	267.02	2669.12	5.5	2323.35	21.2	2396.73	17.5	2090.17	34.76	2466.51	14.2	1474.75	90.99	11858.46	76.24	2370.29	18.8
N	3242.47	739.31	338.58	2232.88	45.21	2204.03	47.11	2593.59	25.02	2197.89	47.53	2677.14	21.12	1362.78	137.9	9314.33	65.18	2978.83	8.85

4. Conclusion

For both live crude oils, VIT measured MMP was found in close match with slim tube measured MMP that confirms multiple contact miscibility between displaced crude oil and CO_2 gas. While for stock oil samples case, higher variation was observed between VIT and slim tube measured MMPs. This may be because of more stabilized higher heavier ends and resultant lower multiple contacts miscibility between considered crude oils and gas phases.

With respect to considered correlations, it was found that for both studied live crude oil samples, no correlation could predict MMP in close agreement with slim tube determined MMP. It confirms the correlations validity only for particular number of crude oil samples studied during correlations development.

Also VIT is a quick, reproducible and less expensive method compared to more time consuming, irreproducible and most expensive slim tube technique. Since, its predicted MMP results, especially for live crude oils, resembles more closely to slim tube determined MMP results, it appears a reliable alternative for accurate MMP determination for any proposed CO_2 injection process. With respect to stock tank oils MMP determination using this technique, further investigation is needed to elaborate the crude oil heavier fraction stabilization / destabilization conditions related to multiple contacts miscibility development through utilizing different API gravity crude oils.

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Appendix A

A.1. Crude oil – CO_2 Correlations

A.1.1. Cronquist Correlation

$$MMP = 16T^{(0.744+0.0015X_{Vol}+0.0011MW_{C5+})}$$

X_{Vol} = Mole fraction of oil volatile components (C_1, N_2)
MW_{C5+} = *Molecular weight of pentane and heavier fractions of oil*
T = Reservoir temperature

A.1.2. Alston Correlation

$$MMP = 0.000878T^{1.06}MW_{C5+}^{1.78}\left[\frac{X_{Vol}}{X_{Int}}\right]^{0.136}$$

X_{int} = Mole fraction of oil intermediate components (H_2S, CO_2, $C_2 - C_6$)

A.1.3. Glaso Correlation

$$MMP = 180 - 3.404MW_{C7+} + \left(1.700 \times 10^{-9}MW_{C7+}^{3.730}e^{786.8MW_{C7+}^{-1.058}}\right)T$$

$$MMP_{F_R<18} = 2947.9 - 3.404MW_{C7+} + \left(1.700 \times 10^{-9} MW_{C7+}^{3.730} e^{786.8MW_{C7+}^{-1.058}}\right)T - 121.2$$

F_R = Mole fraction from C_2 to C_6 of crude oil

MW_{C7+} = Molecular weight of heptane plus fraction of crude oil

A.1.4. Lee Correlation

$$MMP = 7.3924 \times 10^{2.772-[1519/(492+1.8T_R)]}$$

A.1.5. Yelling and Metcalfe Correlation

$$MMP = 12.6472 + 0.01553(1.8T_R + 32) + 1.24192 \times 10^{-4(1.8T_R+32)^2} - \frac{716.9427}{(1.8T_R + 32)}$$

A.1.6. Orr – Jensen Correlation

$$MMP = 0.101386\, exp\left[10.91 - \frac{2015}{255.372 + 0.5556(1.8T_R + 32)}\right]$$

A.1.7. Emera and Sarma Correlation

$$MMP = 5.0093 \times 10^{-5}(1.8T_R + 32)^{1.164}(MW_{C5+})^{1.2785}\left(\frac{X_{Vol}}{X_{int'}}\right)^{0.1073}$$

When bubble point pressure, $P_b < 0.345$ MPa

$$MMP = 5.0093 \times 10^{-5}(1.8T_R + 32)^{1.164}(MW_{C5+})^{1.2785}$$

$X_{int'}$ = Mole fraction of oil intermediate components (H_2S, CO_2, $C_2 – C_4$)

A.1.8. Yuan et al. Correlation

$$MMP = a_1 + a_2 MW_{C7+} - a_3 X_{int} + \left(a_4 + a_5 MW_{C7+} + a_6 \frac{X_{int}}{MW_{C7+}^2}\right)(1.8T_R + 32) + (a_7 + a_8 MW_{C7+} - a_9 MW_{C7+}^2 - a_{10} X_{int})(1.8T_R + 32)^2$$

Whereas, the empirical coefficients are given as

$a_1 = -9.8912$, $a_2 = 4.5588 \times 10^{-2}$, $a_3 = -3.1012 \times 10^{-1}$, $a_4 = 1.4748 \times 10^{-2}$, $a_5 = 8.0441 \times 10^{-4}$

$a_6 = 5.6303 \times 10^{1}$, $a_7 = -8.4516 \times 10^{-4}$, $a_8 = 8.8825 \times 10^{-6}$, $a_9 = -2.7684 \times 10^{-8}$

$a_{10} = -6.3830 \times 10^{-6}$

A.1.9. Shokir Correlation

$$MMP = -0.068616Z^3 + 0.31733Z^2 + 4.9804Z + 13.432$$

Whereas, for pure CO_2 injection

$$Z = \sum_{i=1}^{4} Z_i$$

and

$$Z_i = A3_i y_i^3 + A2_i y_i^2 + A1_i y_i + A0_i$$

Where the subscript 'i' in y_i corresponds to one of the four input variables and A3i – $A0_i$ are the polynomial coefficients in the following way

$y_1 = T_R$, $A3_1 = 2.3660 \times 10^{-6}$, $A2_1 = -5.5996 \times 10^{-4}$, $A1_1 = 7.5340 \times 10^{-2}$, $A0_1 = -2.9182$

$y_2 = X_{Vol}$, $A3_2 = -1.3721 \times 10^{-5}$, $A2_2 = 1.3644 \times 10^{-3}$, $A1_2 = -7.9169 \times 10^{-3}$, $A0_2 = -0.31227 \times 10^{-1}$

$y_3 = X_{int'}$, $A3_3 = 3.5551 \times 10^{-5}$, $A2_3 = -2.7853 \times 10^{-3}$, $A1_3 = 4.2165 \times 10^{-2}$, $A0_3 = -4.9485 \times 10^{-2}$

$y_4 = MW_{C5+}$, $A3_4 = -3.1604 \times 10^{-6}$, $A2_4 = 1.9860 \times 10^{-3}$, $A1_4 = -3.9750 \times 10^{-1}$, $A0_4 = 25.4$

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